Developing an Ab Initio Toolbox to Study Trap States in Quantum Dots

Ezra Alexander Van Voorhis Group, MIT

The performance of semiconductor nanocrystal quantum dots is limited by nonradiative charge recombination arising from a class of poorly understood electronic states known as trap states. Due to their large but finite size, quantum dots remain outside the range of traditional *ab initio* electronic structure methods, with even the smallest realistically-sized quantum dots being infeasible with anything other than ground-state density functional theory (DFT). Here, we present a series of approaches for circumventing this bottleneck to gain insight into quantum dot trapping. First, we present a procedure to identify information about trap states from ground-state DFT calculations, and leverage calculations over a large dataset to gain insight into the trap states in InP and GaP QDs. Second, we discuss a framework for computing X-ray photoelectron spectra of QDs through the Δ SCF formulism. Finally, we introduce a method, BYND, for computing entire excitation spectra of systems of QD size and beyond by combining real-time TD-DFT and the small-matrix approximation.

Hybridization of Moiré States in Twisted Bilayer hBN

Arsineh Apelian University of California, Santa Barbara, Materials Department

Twisted van der Waals structures attracted immense attention in recent years. Often, these systems invoke the concept of strongly localized excitations (quasiparticles (QP's)), i.e. charged electrons, holes, or excitons, subject to a periodic potential landscape whose energy and spatial distribution is determined by the twisting angle applied. Guiding the development of moiré platforms necessitates quantitative theoretical understanding of their properties, however, computing these systems from first principles is a challenging task since large supercells with thousands of atoms are necessary to properly describe the moiré superlattice. Typically, a local approximation is taken where the QP's in the twisted bilayers are subject to a local potential landscape formed by just the distinct stacking orders in the 2D lattice. This picture is invoked e.g., in the description of effective exciton potentials from the variation of the local band gaps. To what extent the non-local long-range interactions modify this picture and how the individual QPs (de)localize in the moiré potential, however, remains unknown. Moreover, calculations are limited to mean-field methods and the role of non-local correlations on the spatial extent of Dyson orbitals are, therefore, also unknown.

Here, we overcome these computational difficulties and investigate the QP landscapes by employing the GW approximation in the stochastic many-body perturbation theory (MBPT) formulation. We extend the technique for determining the Dyson orbitals via a stochastic compression, enabling calculations of QP states in large nanoscale systems. For simplicity, we investigate twisted hexagonal boron nitride (t-hBN) and consider four small twist angles: 2.45° , 2.86° , 3.48° and 5.09° , with structures containing up to ~18,000 electrons. Our results reveal how localized moiré states hybridize with each other and lead to a nontrivial interplay between local structure and non-local correlations. We find that the local gap variation is greatly exaggerated, significantly changing the excitonic potential. For most twist angles, the non-local interactions lead to band-edge QP state mixing (hybridization), which is suppressed for angles around 3.48° . This behavior is mostly determined by the strength of interactions and the localization in the high symmetry regions of the moiré cell.

Structural, mechanical, and electronic properties of BCC refractory binary alloys: A first-principles study

S. Bijjala^a, P. Kumar^a, and Susan R. Atlas^{b,c}

^aDepartment of Mechanical Engineering, University of New Mexico, Albuquerque, NM 87131 ^bDepartment of Chemistry and Chemical Biology, University of New Mexico, Albuquerque, NM 87131 ^cDepartment of Physics and Astronomy and Center for Quantum Information and Control, University of New Mexico, Albuquerque, NM 87131

Abstract

Multicomponent refractory high-entropy alloys (RHEAs) with compositional complex microstructure can offer superior high-temperature mechanical properties compared to the conventional alloys. However, exploring the vast number of RHEAs compositions and their respective properties is a significant challenge. First-principles density functional theory (DFT) methods provide a quantum-level approach for exploring the vast design space offered by complex RHEA systems. To enable the efficient exploration of the combinatorically-complex design space of 5+ element RHEA using machine learning (ML) techniques, we have performed DFT calculations on the relevant unary and binary systems. This approach takes advantage of the known correlation of results obtained from simpler systems in predicting properties of complex alloys [1]. The atomic and electronic insights derived from these composition-structure-property relationships enable the identification of key features/principles for ML design strategies. We present results for structural and electronic properties (lattice constants and formation energies) and mechanical properties (elastic constants) calculated for MoNb, MoTa, MoW, NbTa, WNb and WTa BCC refractory binary alloys. Initial benchmarking studies were performed to establish the methodology and computational parameters for Mo, Nb, Ta and W. Computed properties using d, p and s valence electron-norm-conserving pseudopotentials [6] and using the Perdew-Burke-Ernzerhof (PBE) exchange-correlation energy density functional [7] agree well with other theoretical calculations and with experiment. Special quasi-random structure (SQS) supercells [2,3] were used to represent the disordered binary alloys. The effect of strain due to random arrangement of atoms of different atomic radii in SQS supercells was studied by considering spin and relaxation effects on structural properties. Elastic constants were calculated using density functional perturbation theory with strain perturbation [4]. All calculations were performed using the Abinit DFT electronic structure code [5]. We discuss the computed results in the context of experimental observations.

We would like to thank the UNM Center for Advanced Research Computing, supported in part by the National Science Foundation, for providing the high-performance computing, large-scale storage and visualization resources used in this work. This work was supported in part by NASA EPSCoR Grant # 80NSSC21M0171.

References:

[1] Y.F. Ye, Q. Wang, J. Lu, C.T. Liu, Y. Yang, High-entropy alloy: challenges and prospects, Mat. Today 19, 349 (2016).

[2] A. Zunger, S.-H. Wei, L.G. Ferreira, J.E. Bernard, Special quasirandom structures, Phys. Rev. Lett. 65, 353 (1990).

[3] A. van de Walle, M. Asta, G. Ceder, The alloy theoretic automated toolkit: A user guide, Calphad 26, 539 (2002).

[4] M.J. Verstraete, M. Torrent, F. Jollet, G. Zérah, X. Gonze, Density functional perturbation theory with spin-orbit coupling: Phonon band structure of lead, Phys. Rev. B 78, 045119 (2008).

^[5] X. Gonze, B. Amadon, G. Antonius *et al.*, The Abinit project: Impact, environment and recent developments, Comp. Phys. Comm. **248**, 107042 (2020).

 ^[6] M.J. van Setten, M. Giantomassi, E. Bousquet, M.J. Verstraete, D.R. Hamann, X. Gonze, G.-M. Rignanese, The PseudoDojo: Training and grading a 85 element optimized norm-conserving pseudopotential table, Comp. Phys. Comm. 226, 39 (2018).
 [7] J.P. Perdew, K. Burke, M. Ernzerhof, Generalized gradient approximation made simple, Phys. Rev. Lett. 77, 3865 (1996).

Ferroelectricity, Topological Polarization and Multiferroic Order in van der Waals Materials

Daniel Bennett

John A. Paulson School of Engineering and Applied Sciences, Harvard University (USA)

van der Waals (vdW) materials are emerging as a promising avenue for future applications in nanotechnology. In addition to their useful and tunable electronic, optical, and thermoelectric properties, vdW materials also possess intriguing polar and magnetic properties, opening up new possibilities for the creation of multifunctional nanodevices. Recent studies have illustrated the exceptional ferroelectric properties of vdW materials, outperforming state-of-the-art ferroelectric field effect transistors and paving the way for advancements in nanoelectronics [1]. Additionally, by applying techniques such as twisting or straining to form moiré superlattices, it is possible to engineer networks of polar domains [2-4] with nontrivial topological character [5,6], adding another layer of complexity and potential to these materials.

We employ first-principles methods to elucidate the polar and magnetic properties of vdW materials, which have been instrumental in the understanding of the physical origin of van der Waals ferroelectricity. We provide insights into the formation of polar domains in moiré superlattices and model their response to an electric field, in excellent agreement with experimental observations [3,4]. In addition, using first-principles calculations we discovered the topologically nontrivial nature of the moiré polar domains, forming a network of polar merons and antimerons (half-skyrmions and half-antiskyrmions) [5,6].

Furthermore, we propose a general method for engineering two-dimensional (2D) multiferroics via artificial stacking of van der Waals ferroelectrics [7]. This innovative approach opens up the possibility for the discovery of a wide variety of 2D multiferroics using first-principles methods, setting the stage for the next generation of nanoscale devices.

- [1] Yasuda et. al., Science (2021)
- [2] Ko et. al., Nature Materials (2023)
- [3] Bennett & Remez, npj 2D Materials & Applications (2022)
- [4] Bennett, *Physical Review B* (2022)
- [5] Bennett et. al., Nature Communications (2023)
- [6] Bennett et. al., Physical Review Research (2023)
- [7] Bennett et. al., To Be Submitted

This work has been funded by the US Army Research Office (ARO) MURI project under grant No. W911NF-21-0147 and the Simons Foundation award No. 896626.

The CIDER Framework for Machine Learning Exchange-Correlation Functionals

Kyle Bystrom, <u>Stefano Falletta</u>, <u>Boris Kozinsky</u> Harvard University

This poster provides an overview of the CIDER framework, a machine learning (ML) approach for training exchange-correlation (XC) functionals for Density Functional Theory (DFT). The design of better XC functionals is a central challenge of modern electronic structure theory. However, current developments are limited by the mathematical form of the functional, with efficient semilocal functionals being inaccurate for many technologically important systems and the more accurate hybrid functionals being too expensive for large solid-state systems due to the use of the exact exchange operator. CIDER combines exact constraints and Gaussian process regression to design functionals that are both orbital-dependent and nonlocal, but which can be evaluated at roughly the cost of semilocal functionals and are significantly faster than hybrid DFT in plane-wave codes. To demonstrate this approach, we train an exchange functional and substitute it into existing hybrid functionals to achieve hybrid-DFT accuracy on thermochemical benchmark sets. We also extend the CIDER framework to explicitly fit band gaps and other properties of the DFT eigenvalues. Using this approach, we train an ML functional for the exchange energy that predicts molecular energy gaps and reaction energies of a wide range of molecules in excellent agreement with reference hybrid DFT calculations. To demonstrate the potential of our approach to address challenging materials science problems, we use CIDER functionals to study point defects in semiconductors and polarons in ionic crystals, two types of systems that are plagued by self-interaction error when conventional semilocal functionals are used. Due to its transferability and computational efficiency for both molecular and extended systems, the CIDER framework makes significant progress on overcoming the cost-accuracy trade-off between semilocal and hybrid DFT, and our general approach provides a feasible path toward a universal exchange-correlation functional with post-hybrid DFT accuracy and semilocal DFT cost.

Designing computationally efficient Laplacian-based kinetic energy density functionals

Antonio C Cancio Ball State University Bishal Thapa George Mason University Hector Francisco University of Florida

In recent years interest has grown in the use of the orbital-free kinetic energy density (KED) in density functional theory, either for "deorbitalizing" metaGGA functionals or to remove orbitals entirely from the Kohn-Sham formulation. The Perdew-Constantin (PC) KE metaGGA [1] and later variants demonstrate the effectiveness of the use of the Laplacian of the density to model the transition between the slowly varying electron gas and single-orbital limits in such functionals. Unfortunately, the use of the Laplacian in this context creates unphysically spiky Pauli potentials that are difficult to converge and lead to inherently noisy results. To ameliorate this problem, we construct and test a smoothness measure based on the variational description of Poisson's equation, applied to the Laplacian-generated terms in the potential. Optimization of this measure is used to develop dramatically smoother models of the electron localization transition.

We discuss new smoothed kinetic energy density functionals derived from PC and the recent RPP [2] designed to remove the dependence on kinetic energy of the r2SCAN metaGGA. Applying these to standard test sets of molecules and solids yield performance in predicting structural properties that is on par or better than the parent functional, and, for VASP calculations for solids, does so with consistently less wall time. However, the number of self-consistent steps needed for convergence can be significantly longer for Laplacian=based potentials than for the original orbital-dependent potentials, particularly for molecular dynamics calculations, indicating the existence of instabilities that remain to be resolved.

Work supported by the National Science Foundation under Grant No. DMR-1912618.

- [1] J. P. Perdew and L. A. Constantin, Phys. Rev. B 75, 155109 (2007).
- [2] A Kaplan and J Perdew Phys. Rev. Materials 6, 083803 (2022)

Dynamical Downfolding and Construction of Effective Hamiltonians for Correlated Systems

Annabelle Canestraight University of California, Santa Barbara

There is wide and longstanding interest in reducing the computational cost for electronic structure calculations of correlated systems. Recently, Romanova et. al have developed a method of dynamical downfolding to map a large correlated problem onto a reduced subspace [Romanova et al., npj Computational Materials 9 (1), 126, 2023]. While this work succeeded in finding quantitative agreement with the experimental results, the limitations of this approach have not yet been explored. Using a solvable model system, we investigate under which conditions dynamical downfolding with renormalized 1-body terms can reliably provide a portion of the optical spectrum. Further, we relate this work to the method of exact downfolding by construction of a Schur complement. By studying the exact self-energy, we develop a language to understand how information about the many-body eigenvectors is lost through downfolding.

Modeling High Entropy Oxides with DFT and Statistical Mechanics

<u>Grace Chamberlain</u>, Lily Jade Joyce, Dr. Kendra Letchworth-Weaver James Madison University

High entropy oxides (HEOs) are promising materials for lithium-ion battery cathodes and potential photocatalysts for generation of fuels from sunlight, but experimental discovery and synthesis of new HEOs is expensive and time consuming. These materials have high formation temperatures and become more stable through entropy-driven configurational disorder, so predicting novel HEO compositions with enthalpy-based methods, such as Density Functional Theory (DFT), poses challenges. To overcome these challenges, we created Python-based software which randomizes the placement of atoms in a user-defined lattice type, creating an ensemble of microstates for the local environment of each HEO composition. We use DFT to determine the enthalpy of formation from the single-phase metal oxides for each microstate within the ensemble. Based on the DFT-computed enthalpies of the microstates, we then create a statistical-mechanical model which computes the expectation values and variances of relevant energetic, structural, and electronic properties over the entire ensemble of structures. We explore the sensitivity of our model's predictions to details such as number of microstates and supercell size. For HEOs which experimental groups have synthesized, the efficacy of our approach may be tested by direct comparison to measured formation temperatures as well as bond length distributions determined by X-ray diffraction (XRD) and X-ray absorption spectroscopy (XAS).

Vacancy-induced tunable Kondo effect in twisted bilayer graphene

<u>Yueqing Chang^{1, 2, *}</u>, Jinjing Yi^{1, 2}, Ang-Kun Wu^{1, 2}, Fabian B. Kugler^{3, 1, 2}, Eva Y. Andrei¹, David Vanderbilt^{1, 2}, Gabriel Kotliar^{1, 2, 4}, and J. H. Pixley^{1, 2, 3, †}

¹Department of Physics and Astronomy, Rutgers University, Piscataway, NJ 08854, USA

²Contender Materials Theory Determined University, Fiscalaway, NJ 00054, USA

²Center for Materials Theory, Rutgers University, Piscataway, NJ 08854, USA

³Center for Computational Quantum Physics, Flatiron Institute, 162 5th Avenue, New York, NY 10010,

USA

⁴Condensed Matter Physics and Materials Science Department, Brookhaven National Laboratory, Upton, NY 11973, USA

In single sheets of graphene, vacancy-induced states have been shown to host an effective spin-1/2 hole that can be Kondo-screened at low temperatures. Here, we show how these vacancy-induced impurity states survive in twisted bilayer graphene (TBG), which thus provides a tunable system to probe the critical destruction of the Kondo effect in pseudogap hosts. Ab-initio calculations and atomic-scale modeling are used to determine the nature of the vacancy states in the vicinity of the magic angle in TBG, demonstrating that the vacancy can be treated as a quantum impurity. Utilizing this insight, we construct an Anderson impurity model with a TBG host that we solve using the numerical renormalization group combined with the kernel polynomial method. We determine the phase diagram of the model and show how there is a strict dichotomy between vacancies in the AA/BB versus AB/BA tunneling regions. In AB/BA vacancies, we find that the Kondo temperature at the magic angle develops a broad distribution with a tail to vanishing temperatures due to multifractal wavefunctions at the magic angle. We argue that the scanning tunneling microscopy response in the vicinity of the vacancy can act as a non-trivial probe of both the critical single-particle states and the underlying many-body ground state in magic-angle TBG.

*<u>yueqing.chang@rutgers.edu</u> †jed.pixley@physics.rutgers.edu

Reference: arXiv:2312.09286

Title: Green's function functionals as density functionals

Name: Steven Crisostomo Affiliation: University of California, Irvine

Using exact density functional theory, we formalize a theory of Green's function (GF) functionals. We explore self-energies along traditional lines, as functionals of bare or interacting GFs, and develop a density-functional counterpart, following our recent work [arXiv:2403.03364 (2024)]. The density functional constructions are inherently non-diagrammatic and don't require convergence of an underlying perturbation theory. Keeping careful track of GF and density functional dependence, we examine the self-energy corrections associated with the fixed-density adiabatic connection formalism. Lastly, we derive a density-functional version of the Luttinger-Ward (LW) functional, which differs considerably from the construction first proposed by Sham [*Phys. Rev. B* **32**, 3876 (1985)]. We illustrate exact results using a two-site Hubbard model.

This work is in collaboration with Kieron Burke and Hardy Gross, and is supported by NSF Award No. CHE-2154371.

Ab Initio Approach to Spin-Phonon Coupling in Transition Metal Insulators

Ramesh Dhakal, Samuel Griffith, Kate Choi, and Stephen M. Winter * Department of Physics and Center for Functional Materials, Wake Forest University, Winston-Salem, North Carolina 27109, USA

Within the framework of numerical des Cloiseaux effective Hamiltonians, we introduce a method to compute generic spin-phonon couplings in transition metal insulators. By incorporating lattice degree of freedom and treating phonon as genuine dynamical variable within the low energy space, we compute arbitrary multipole-phonon couplings with full q-dependence. One key advantage of this approach is its ability to provide a comprehensive estimation of spin-phonon coupling, including "Raman" coupling that is required for the evaluation of phonon Hall effect [1], at a relatively modest computational expense. We benchmark this method for MnPSe3, a layered honeycomb material, to reproduce temperature-dependent damping of phonon Raman lineshapes[2].

L. Sheng, D. Sheng, and C. Ting, Phys. Rev. Lett. 96, 155901 (2006)
 T. T. Mai, K. F. Garrity, A. McCreary, J. Argo, J. R. Simpson, V. Doan-Nguyen, R. V. Aguilar, and A.

R. H.Walker, Sci. Adv. 7, eabj3106 (2021)

Reaction and Ion Transport at Solid-state battery Electrode-electrolyte Interface from Machine Learning Molecular Dynamics

Jingxuan Ding, Menghang Wang, Laura Zichi, Albert Musaelian, Yu Xie, Anders Johansson, Simon Batzner, Boris Kozinsky School of Engineering and Applied Science, Harvard University, Cambridge, MA

Atomistic-level understanding of the chemical reactions forming the solid-electrolyte interphase (SEI) in solid-state lithium batteries has remained challenging, primarily due to the limited resolution in experimental techniques and the insufficient accuracy in large-scale simulations. In this work, we combine on-the-fly active learning based on Gaussian Process regression (FLARE) with local equivariant neural network interatomic potentials (Allegro) to construct a machine-learning force field (MLFF) to perform large-scale long-time explicit reactive simulation of a complete symmetric battery cell with ab initio accuracy. The MLFF is validated with experimental values of mechanical properties of bulk lithium and diffusion coefficient of solid electrolyte. For the symmetric battery, we observe prominent fast reactions at the interface and characterize the dominant reaction products along with their evolution time scales, using unsupervised learning techniques based on atomic geometry descriptors. Our simulation reveals the kinetics and the passivation involved in the chemical reaction responsible for the SEI formation. The methods in this study are promising for acceleration analysis of atomistic mechanisms in complicated heterogeneous systems and provide design insights for the development of solid-state batteries.

Unified Differentiable Learning of Materials Dielectric and Ferroelectric Responses

Stefano Falletta,¹ Andrea Cepellotti,¹ Anders Johansson,¹ Chuin Wei Tan,¹ Albert Musaelian,¹ Cameron J. Owen,² and Boris Kozinsky^{1,3}

¹ John A. Paulson School of Engineering and Applied Sciences, Harvard University, Cambridge MA, USA

² Department of Chemistry and Chemical Biology, Harvard University, Cambridge MA, USA

³ Robert Bosch LLC Research and Technology Center, Watertown, MA, USA

Modelling material responses to external stimuli is a primary objective of computational materials science. However, current methods are limited to small-scale simulations due to the unfavorable scaling of computational costs. Here, we propose a machine-learning formulation where response properties stem from derivatives of a generalized potential function of atomic coordinates and applied external fields. Focusing on responses to electric fields, the method predicts electric enthalpy, forces, and dielectric responses within a unified equivariant model enforcing exact physical constraints, symmetries and conservation laws. Through application to α -SiO₂, we demonstrate that our approach can be used for predicting vibrational and dielectric properties of materials, and for conducting large-scale dynamics under arbitrary electric fields. We then apply our method to BaTiO₃ and determine the temperature-dependent ferroelectric hysteresis and the underlying dynamics of ferroelectric domains, thus going beyond the reach of standard quantum mechanical methods.

[1] S. Falletta, A. Cepellotti, A. Johansson, C. W. Tan, A. Musaelian, C. J. Owen, B. Kozinsky, arXiv:2403.17207 (2024)

Significance of Structural Disorder For Charge Dynamics in θ-(ET)₂X Materials

Owen Ganter¹, Stephen Winter¹

¹Department of Physics and Center for Functional Materials, Wake Forest University, Winston-Salem,

North Carolina 27109, USA

 θ -ET₂X materials are model two dimensional correlated electron systems known to exhibit a variety of electronic phenomena resulting from their frustrated inter-site Coulomb repulsions including charge ordered, glassy, and metallic states. The materials have drawn attention^{1,2} in recent years particularly as to the phenomenon of charge vitrification and melting. In this study we consider the impact of structural disorder in the ethylene end groups (EEGs) of individual ET molecules for the charge dynamics in the bulk material. We computed electronic phase diagrams as a function of the inter-site coulomb repulsions and transfer integrals using a combination of Density Functional Theory (DFT) and Density Matrix Embedding Theory³ (DMET). We find that the bulk electronic properties are significantly affected by the in-stack transfer integral, and that variation within this parameter caused by EEG disorder could be sufficient to induce local regions of metallic and crystallized charge states. This finding supports the hypothesis that EEG disorder can enhance charge glassiness, thus illustrating the importance of disorder in structural and electronic degrees of freedom in the physics of θ -(ET)₂X materials.

References

[1] Sasaki, S. et al., Science 357,1381-1385 (2017)

[2] Sato, T. et al., Nature Mater. 18, 229–233 (2019)

[3] Knizia, G. et al., Phys. Rev. Lett. 109(18), 186404 (2012)

High-order harmonic generation in graphene quantum dots in the field of an elliptically polarized optical pulse

Suresh Gnawali and Vadym Apalkov

Department of Physics and Astronomy, Georgia State University, Atlanta, Georgia 30303, USA

We study theoretically the generation of high-order harmonics in graphene quantum dots placed in the field of an elliptically polarized ultrashort pulse. The generated high-order harmonics are sensitive to the pulse's ellipticity and amplitude. The intensities of high-order harmonics become very sensitive to the ellipticity of an incident pulse when its polarization gets close to a circular one, and some high-order harmonics become strongly suppressed for a circularly polarized incident pulse. The suppressed harmonic orders depend on the symmetry of the quantum dot systems. Every third harmonic is suppressed for triangular quantum dots, which have D_{3h} symmetry. In contrast, for hexagonal quantum dots with D_{6h} symmetry, such suppression is observed for every sixth harmonic, and the even-order harmonics are suppressed for all ellipticities of the incident pulse due to an additional inversion symmetry of the hexagonal quantum dots. The ellipticities of the generated high-order harmonics also show strong nonmonotonic dependence on the ellipticity of an incident pulse, in which the dependence becomes stronger for high pulse amplitudes.

Recent Progress in the Rappe Group: Bulk Photovoltaic Effect and Catalysis in Li-CO₂ Batteries

Andreas Ghosh and Peter Bazianos Department of Chemistry, University of Pennsylvania

In this poster we present some recent progress in research by the Rappe Group, a computational materials chemistry group at the University of Pennsylvania. We focus on the Bulk Photovoltaic Effect (BPVE), the generation of DC photocurrent in materials without inversion symmetry, and the catalytic activity of graphene-based cathodes in Li-CO₂ batteries, as well as the electronic structure methods used to calculate these phenomena.

Tight-binding models provide great insight and are a low-cost alternative to ab initio methods for calculation of a material's electronic structure. These models are used to calculate optical responses, including nonlinear optical effects such as the shift current in the bulk photovoltaic effect. The validity of tight-binding models is often evaluated by comparing their band structures to those calculated with DFT. However, we find that band structure agreement is a necessary but not sufficient condition for accurate optical response calculations. We compute shift current responses for a variety of tight-binding models of MoS₂, including both Slater-Koster and Wannier tight-binding models that treat the Mo 4*d* orbitals and/or S 3*p* orbitals. We also truncate hoppings in the Wannier function models to next-nearest neighbor, as is common in tight-binding models, in order to gauge the effect on optical response. We establish that both band structure agreement and wavefunction agreement are required to accurately model optical response.

The Li-CO₂ battery is a promising energy storage system with impressive theoretical specific energy and discharge capacity. Graphene-based single-atom catalysts (SAC) are among the most promising cathode catalysts, but these batteries continue to have high reaction barriers. Through DFT calculations, we identify improvements to the heavily studied FeN₄-SAC graphene catalyst, using solvation models to assess solvent impact. We propose enhancing the SAC by using a Ti metal center, which is found to stabilize high-energy intermediates in the reaction mechanism. This improvement is due to more active Ti 3*d* orbitals, identified with partial density of states calculations, and stronger bidentate interaction with adsorbates. Additionally, polar ligands show promising capability to modulate electron density of the SAC to induce favorable changes in adsorbate structure. These cathode materials are promising innovations for Li-CO₂ batteries and can help them reach their full potential as highly energy-dense storage systems.

Designing Point Defects with Low Electron-Phonon Coupling in 2D Materials

Fatimah Habis^{1,2}, Yuanxi Wang¹ ¹Department of Physics, University of North Texas, Denton, TX 76203, USA ²Department of Physics, Jazan University, Jazan 82817, Saudi Arabia

Point defects in semiconductors are promising for quantum information science applications due to their ability to form well-localized states within the band gap, acting as isolated atoms that can be utilized as single photon emitters (SPEs) and spin qubits. A key factor for higher photon indistinguishability, essential for effective SPEs, is small electron-phonon coupling, often measured by Huang-Rhys (HR) factors. Calculating HR factors is complex, and their numerical values are typically used without establishing a meaningful link to the physical defect system. Identifying this link could guide the design of defects to minimize HR factors.

We propose that small HR factors correspond to the preservation of bonding-character between the initial (occupied) and final (unoccupied) states in a transition. We demonstrate this for realistic SPE candidates in hBN defect systems and diamond NV centers. HR factors are calculated using first-principles within the one-dimensional configuration coordinate diagram (1DCCD) approximation and compared with full phonon spectra calculations. These calculations involve extrapolating spectral functions towards the dilute defect limit using an embedding method that relies on the limited range of interatomic force constants in covalent semiconductors. The calculated HR factors are then correlated with the bonding-character similarity between the excited and ground states.

Combined ARPES and DFT+eDMFT investigation on high-temperature topological superconductivity in the FeTe_xSe_{1-x} system

<u>Christopher Jacobs</u> and Subhasish Mandal West Virginia University Department of Physics and Astronomy

H. Lin, C.Yan, Q. Gao, G. Berruto, and S. Yang University of Chicago Pritzker School of Molecular Engineering

So far, most of the studies of topological materials have focused on the single-particle regime where traditional band theory accurately reproduced experimental findings. A fundamentally unaddressed question is how strong electron-electron interactions drive a topological system far from the single-particle limit where electrons are close to being localized. Recently, the strongly correlated Fe(Te, Se) systems have been a point of interest in the literature as it is a potential system to exhibit high-temperature topological superconductivity. We use a combination of *ab initio* embedded dynamical mean-field theory (eDMFT), molecular beam epitaxial (MBE) growth, and time and angle-resolved-photoemission-spectroscopy (trARPES) to understand the correlated electronic structure and vibrational properties of the Fe(Te,Se) system under an applied in-plane strain. Using eDMFT, we compute structural parameters for various $FeTe_xSe_{1-x}$ systems including the chalcogen heights and the important A_{1g} phonon mode. In addition, we explore the effects of spin-orbit coupling and temperature to gain more insight into the topological phase transition, the nature of the hybridization, and the transition to the orbital-selective correlated phase. Computed eDMFT orbital-resolved spectral functions are found to be in excellent agreement with the ARPES data. Our combined ARPES + eDMFT approach unravels an interesting phase diagram of the Fe(Te, Se) system between superconductivity and topological non-trivial phase as a function of increasing electron correlation.

Two-dimensional topological superconductivity with Rashba type pairing in 1T'-WS₂/2H-WS₂ heterophase bilayer

Xuance Jiang,^{1, 2} Yuan Ping,^{3, 4} Yafis Barlas,⁵ and Deyu Lu¹ ¹Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, NY 11973, USA ²Department of Physics and Astronomy, Stony Brook University, Stony Brook, NY 11794, USA ³Department of Materials Science and Engineering, University of Wisconsin-Madison, WI, 53706, USA ⁴Department of Physics, University of California, Santa Cruz, CA, 95064, USA ⁵Department of Physics, University of Nevada, Reno, 1664 N. Virginia Street, Reno, NV 89557, USA

Topological superconductors with Rahshba-type pairing can host fascinating electron properties, which may lead to applications in quantum information science Based on first-principles calculations, we propose a candidate system, the $1T'-WS_2/2H-WS_2$ heterophase bilayer, that exhibits topological superconductivity with broken inversion symmetry. We find that the electron doping from the 2H-WS₂ layer to the $1T'-WS_2$ layer creates an interface dipole and induces Rashba band splitting. The hybridization between 1T' and 2H phase shifts the valence bands and increases the Fermi density of states. Using *ab initio* calculation, we find that the electron-phonon coupling and superconductivity in heterophase bilayer is enhanced compared to monolayer. The low energy band dispersion is reproduced by a minimal six-band k·p Hamiltonian. Our work demonstrates that by exploring different combinations of transition-metal dichalcogenide materials and phases, one can achieve novel topological superconducting properties in van der Waals heterostructures of 2D materials.

Energy-lowering structural distortions in cuprates: impact on crystal and electronic structures

Zheting Jin and Sohrab Ismail-Beigi Yale University

A comprehensive description of cuprates is particularly challenging due to the interplay of strong electronic interactions and complex crystal structures. While strong electronic correlations can be captured by manybody methods such as density matrix renormalization group (DMRG) and quantum Monte Carlo (QMC), prior works often utilize idealized Hamiltonians that dismiss structural complexities [1-2]. However, realistic structural distortions can lead to significant effects such as symmetry breaking and spatial variations in superconducting gaps [3-4] which are not captured in simplified models.

Reliable structure predictions can be provided by first-principle calculations. We apply density functional theory (DFT) to provide a realistic description of the normal state of the cuprate Bi-2212 (Bi₂Sr₂CaCu₂O_{8+x}), focusing on its structural, electronic, and magnetic properties. Our approach emphasizes the crucial role of structural distortions that lower the energy of the system, allowing us to: (a) accurately describe the experimentally observed insulating antiferromagnetic (AFM) ground state of the undoped parent compound (in contrast to the metallic state predicted by previous *ab initio* studies); (b) identify numerous low-energy competing spin and charge stripe orders in the hole-overdoped (x=0.25) material that are nearly degenerate in energy with the AFM ordered state, indicating strong spin and charge fluctuations; (c) predict the lowest-energy hole-doped x=0.25 crystal structure that exhibits long-range structural distortions and whose predicted oxygen dopant positions match high-resolution scanning transmission electron microscopy (STEM) measurements; and (d) describe electronic bands near the Fermi energy with flat antinodal dispersions and Fermi surfaces that in agreement with angle-resolved photoemission spectroscopy (ARPES) measurements and provide a clear explanation for the structural origins of the so-called ``shadow bands''.

Through these findings, we demonstrate how critical the inclusion of realistic structural details is for the accurate modeling of complex materials such as Bi-2212, paving the way for more accurate many-body studies and a deeper understanding of the superconducting properties.

This work was supported by grant NSF DMR 2237469, NSF ACCESS supercomputing resources via allocation TG-MCA08X007, and supercomputing resources from Yale Center for Research Computing.

References

[1] Z.-H. Cui, C. Sun, U. Ray, B.-X. Zheng, Q. Sun, and G. K.-L. Chan, Physical Review Research 2, 043259 (2020)

[2] S. R. White and D. Scalapino, Physical Review B 92, 205112 (2015)

[3] K. McElroy, J. Lee, J. Slezak, D.-H. Lee, H. Eisaki, S. Uchida, and J. Davis, Science 309, 1048 (2005)

[4] B. M. Andersen, P. Hirschfeld, and J. A. Slezak, Physical Review B 76, 020507 (2007)

Materials Discovery using Machine Learning and DFT for Interconnects

Lily Jade Joyce Rensselaer Polytechnic Institute

As the dimensions of semiconductors in computing technologies continue scaling down, the dimensions of the wires connecting them must scale down as well. Traditional wires have become less viable at the nano-scale because the resistivity of typical conductors such as copper increases dramatically as dimensions scale down. Previous studies show that this effect can be reduced by directional conductors with highly anisotropic Fermi velocities[1]. However, the amount of materials that are able to outperform copper at small dimensions remains low. Using the previous work as a training dataset, we utilize machine learning (ML) models to predict the resistivity scaling for thousands of unseen materials. We validate the ML predictions using DFT and evaluate electron-phonon scattering for the most promising candidates to map their overall resistivity as a function of dimension. We identify 29 new materials that can potentially outperform copper at ~10nm and below.

[1] S. Kumar, C. Multunas, B. Defay, D. Gall and R. Sundararaman, "Ultralow electron-surface scattering in nanoscale metals leveraging Fermi-surface anisotropy", *Phys. Rev. Mater.* **6**, 085002 (2022)

doped: Python toolkit for robust and repeatable charged defect supercell calculations

Seán R. Kavanagh Harvard University

Defects are a universal feature of crystalline solids, dictating the key properties and performance of many functional materials. Given their crucial importance yet inherent difficulty in measuring experimentally, electronic structure methods are widely used to predict defect behaviour at the atomic level and the resultant impact on macroscopic properties. Here we report *doped*,¹ a Python package for the generation, pre-/post-processing and analysis of defect supercell calculations. *doped* has been built to implement the defect simulation workflow in an efficient, user-friendly yet powerful and fully-flexible manner, with the goal of providing a robust general-purpose platform for conducting reproducible calculations of solid-state defect properties.

Beyond the core functionality of *doped* in generating defect supercells and competing phases, writing calculation input files, parsing calculation outputs and analysing/plotting defect-related properties, some key advances include:

- Efficient supercell generation outperforming widely-used & established algorithms.

- Efficient charge-state estimation, outperforming the most widely-used current approaches in terms of accuracy and efficiency.

- Efficient competing phase selection based on controllable error tolerances.

- Automated symmetry & degeneracy handling for defect thermodynamics & analysis

- Automated compatibility checking & calculation sanity checking

- Streamlined thermodynamic analysis; formation energy diagrams, (non-)equilibrium Fermi level solving,

doping analysis, Brouwer-type diagrams, 2D temperature & chemical potential heatmaps...

- Finite-size corrections; both the isotropic Freysoldt (FNV)² and anisotropic Kumagai (eFNV)³ - Reproducibility & tabulation; natively supports & encourages reproducibility (all I/O JSONable aiding provenance tracking, tabulated summary outputs...)

- Native compatibility with high-throughput architectures (AiiDA⁴, atomate(2)⁵...) and other python-based defect analysis codes (ShakeNBreak⁶, easyunfold⁷, nonrad⁸, CarrierCapture.jl⁹, pydefect¹⁰...)

Some additional features include directional-dependent site displacement (local strain) analysis, deterministic & informative defect naming, molecule generation for gaseous competing phases, multiprocessing for expedited generation & parsing, shallow defect analysis (via *pydefect*¹⁰), Wyckoff site analysis (including arbitrary/interstitial sites), controllable defect site placement to aid visualisation and more. The functionality and recommended usage of *doped* is demonstrated in the tutorials (https://doped.readthedocs.io/en/latest/Tutorials.html) on the documentation website (https://doped.readthedocs.io/en/latest/).

¹ S. R. Kavanagh, A. G. Squires, A. Nicolson, I. Mosquera-Lois, A. M. Ganose, B. Zhu, K. Brlec, A. Walsh and D. O. Scanlon, doped: Python toolkit for robust and repeatable charged defect supercell calculations, *Journal of Open Source Software*, 2024, 9, 6433.

² C. Freysoldt, J. Neugebauer and C. G. Van de Walle, Fully *Ab Initio* Finite-Size Corrections for Charged-Defect Supercell Calculations, *Phys. Rev. Lett.*, 2009, **102**, 016402.

Y. Kumagai and F. Oba, Electrostatics-based finite-size corrections for first-principles point defect calculations, Phys. Rev. B, 2014, 89, 195205.

⁴ S. P. Huber, S. Zoupanos, M. Uhrin, L. Talirz, L. Kahle, R. Häuselmann, D. Gresch, T. Müller, A. V. Yakutovich, C. W. Andersen, F. F. Ramirez, C. S. Adorf, F. Gargiulo, S. Kumbhar, E. Passaro, C. Johnston, A. Merkys, A. Cepellotti, N. Mounet, N. Marzari, B. Kozinsky and G. Pizzi, AiiDA 1.0, a scalable computational infrastructure for

automated reproducible workflows and data provenance, *Scientific Data*, 2020, 7, 300.
 K. Mathew, J. H. Montoya, A. Faghaninia, S. Dwarakanath, M. Aykol, H. Tang, I. Chu, T. Smidt, B. Bocklund, M. Horton, J. Dagdelen, B. Wood, Z.-K. Liu, J. Neaton, S. P. Ong, K. Persson and A. Jain, Atomate: A high-level interface to generate, execute, and analyze computational materials science workflows, *Computational Materials*

Science, 2017, 139, 140–152.
 I. Mosquera-Lois, S. R. Kavanagh, A. Walsh and D. O. Scanlon, ShakeNBreak: Navigating the defect configurational landscape, Journal of Open Source Software, 2022, 7, 4817.

B. Zhu, S. R. Kavanagh and D. Scanlon, easyunfold: A Python package for unfolding electronic band structures, *Journal of Open Source Software*, 2024, 9, 5974.
 M. E. Turiansky, A. Alkauskas, M. Engel, G. Kresse, D. Wickramaratne, J.-X. Shen, C. E. Dreyer and C. G. Van de Walle, Nonrad: Computing Nonradiative Capture Coefficients from First Principles, *arXiv:2011.07433 [cond-mat].*

S. Kim, S. N. Hood, P. van Gerwen, L. D. Whalley and A. Walsh, CarrierCapture.jl: Anharmonic Carrier Capture, *Journal of Open Source Software*, 2020, 5, 2102.
 Y. Kumagai, N. Tsunoda, A. Takahashi and F. Oba, Insights into oxygen vacancies from high-throughput first-principles calculations, *Phys. Rev. Materials*, 2021, 5, 123803.

Automated Active Space Selection for Molecules and Complexes with Dipole Moments

Benjamin Kaufold^a, Sijia Dong^{a,b}

^{a.} Department of Chemistry, Northeastern University, Boston, MA 02115

^{b.} Department of Physics and Department of Chemical Engineering, Northeastern University, Boston,

MA, 02115

Multireference methods are important methods to describe strongly correlated molecular systems. However, the selection of active space for multireference methods is non-trivial, and a "bad" active space can result in unphysical results. In this work, we use a physical observable, the dipole moment, to guide the selection of active spaces. We developed an automated active space selection approach based on the accuracy of dipole moments to systematically select the active space for organic molecules, metal oxides, and weakly-associated molecular complexes with long-range charge transfer for high-throughput multireference calculations. We demonstrated that the approach is effective in describing the low-lying excitations, charge-transfer states, and transition metal spin states with reasonable accuracy when used for complete active space 2nd-order perturbation theory and multiconfiguration pair-density functional theory.

Friction of Alumina Borate from Molecular Dynamics Simulations: A Lubricant for Space Exploration

Sung-Yup Kim¹, Adri van Duin² and Eunja Kim¹ Department of Physics University of Texas at El Paso (UTEP)¹ Department of Mechanical Engineering Pennsylvania State University²

Alumina borate, formulated as $10Al_2O_3 \cdot 2(B_2O_3)$, emerges as a promising solid lubricant for space exploration due to its remarkable hardness and reduced coefficient of friction (COF). Within this study, we explored the lubricating dynamics of boron trioxide (B_2O_3) —a glass-forming compound known for its friction-minimizing properties when it transitions into a glassy layer. Utilizing ReaxFF molecular dynamics (MD) simulations, we examined how COF evolves with various velocities and temperatures. The simulation setup involved a dual-layer coating of B_2O_3 on both upper and lower Al_2O_3 substrates, with alumina borate inserted between them as a lubricant. To accurately simulate chemical reactions, we employed recently developed Al/B/O ReaxFF parameters. Moving velocities from 0.1 m/s to 20 m/s were applied to the upper substrate, with temperatures would increase COF, our findings reveal that COF initially rises before diminishing across these variables. Notably, specific combinations of velocities and temperatures were identified as critical factors contributing to elevated COF levels.

This research was funded by NASA CAN, grant number NV-80NSSC20M022.

Twisted Bilayer Graphene Electronic Structure Revisited

Daniel T. Larson Harvard University

We study the low-energy bands of twisted bilayer graphene (TBG), summarizing the configuration space approach that allows for the construction of an *ab initio* tight binding hamiltonian. We find that the bands are never perfectly flat and the Fermi velocity never vanishes, but rather a "magic range" of twist angles exists where the lower band becomes extremely flat and the Fermi velocity attains a nonzero minimum value. Motivated by features related to the atomic relaxation in the moiré pattern, namely, circular regions of AA stacking, triangular regions of AB/BA stacking, and linear domain walls separating the latter, we endeavor to build effective tight binding models on the moiré scale that can capture the changes in the low energy bands as a function of twist angle.

Study of sodium containing layered oxides for battery applications: Defect control to enhance ionic conductivity

Daisy Lopez¹, Yohannes Getahun¹, Danniella Vera¹, Alan Cangas¹, Oscar Buenrostro¹, Hari Nair¹, Eunja Kim¹

¹Department of Physics, 500 W University Ave, The University of Texas at El Paso, El Paso, TX 79968,

USA

Abstract: The goal of this project is to develop sodium-containing novel layered honeycomb oxides for solid state battery cathodes. A combined experimental and theoretical effort was undertaken by our team to discover alternatives to replace critical elements like lithium (Li) and cobalt (Co) which are currently routinely used in solid state secondary batteries for energy storage. An economically and environmentally viable solution is to use sodium (Na) or other alkalis to replace the critical elements. We explored the family of compounds A_2M_2 TeO₆ (A = alkali, M = transition metal) in this project. Our preliminary results include successful synthesis of several Na₂Ni₂TeO₆-derived compounds with varying Na content (i.e. cationic vacancies) and substitutions (ex. Zn replacing Na). The motivation for the chemical tuning is the close connection between defect structure and ionic conductivity in the proposed compounds. We are working on the quantification of the optimal Na-content for highest ionic conductivity in the proposed compounds. Density functional theory (DFT) calculations were carried out to investigate the most favorable chemical coordination around Na ions which supports optimal ionic conduction. Our preliminary DFT result shows good agreement between calculated and measured lattice constants, predicting the bulk modulus to be 98 GPa and 97 GPa for Na₂Ni₂TeO₆ and Na₃Ni₂TeO₆, respectively. DFT calculations for three different sodium sites (i.e., Na1, Na2, and Na3) in Na2Ni2TeO6 were conducted. Our results indicate that Na atoms in the Na1 site are energetically more favorable than the ones either in Na2 or in Na3 sites. This finding agrees well with the measured XRD data. Structural and magnetic properties were also investigated.

Lithium doping effects on electron-phonon properties of Bi₂Sr₂CaCu₂O₈

Jiaji (Bruce) Ma

Department of Applied Physics, Yale University

The origin of unconventional high-temperature superconductivity in cuprate metal oxides is still a subject of ongoing research. Within the BCS theory framework and its generalization by Eliashberg, the introduction of high-frequency phonons, through methods such as doping light elements like lithium, can lead to stronger electron-phonon coupling and hence higher superconducting transition temperature. Drawing on these ideas, our study explores the effects of Lithium doping on the electron-phonon interactions in cuprates. We choose Bi₂Sr₂CaCu₂O₈ (BSCCO, Bi-2212) as a prototypical cuprate and investigate how its structural, electronic, phononic and electron-phonon properties are affected by Li-Bi substitution. Full-Brillouin-zone electron-phonon calculations are highly time-consuming even with highlevel parallelization. Here we present an economical method to calculate electron-phonon coupling, which has enabled an analysis on the atom, mode, and layer-resolved electron-phonon coupling for Li-Bi substitution.

The electronic properties of sulfur and SOx-based sp3 defects in single-walled carbon nanotubes from first-principles theory

Tina N Mihm

Department of Electrical and Computer Engineering, Boston University, Boston, MA 02215, USA

Semiconducting single-walled carbon nanotubes (SWCNT) containing sp3-defects are promising components in optoelectronic devices because of their bright tunable photoluminescence, long spin coherence, and demonstrated single-photon emission. Modifying the defect functional group leads to highly selective and tunable properties within the SWCNT. We present a first-principles computational study of the chiral (6,5) SWCNT, functionalized by SO₂ and its likely derivatives. Using density functional theory (DFT), we investigate the nature of binding of SO₂ and its four derivatives (S, SO, SO₃, and H₂SO₄) on the SWCNT including the role of hydrogen passivation of the defect site. Our calculations, in comparison with experiment, indicate that SO₂ preferably decomposes to its substituents. We show that the formation of a defect site for SOx-based defects is dependent on both the substituent and the location of binding on the SWCNT.

This work was supported by the DOE Office of Science, Basic Energy Sciences under Award No DE-SC0023402.

Parametrization of a heme-protein conductivity model by DFT and TDDFT

Luke Nambi Mohanam,[#] Rafael Umeda,^{*} Ruqian Wu,^{*} Sahar Sharifzadeh[#] Department of Electrical and Computer Engineering, Boston University[#] Department of Physics, University of California Irvine^{*}

Outer membrane cytochrome-C heme-protein polymers are bio-active electron transport chains for respiration, moving electrons outside of cells towards the final electron acceptor. This long-range electron transport occurs via electron transfer between heme group co-factors covalently attached to the protein. We present two approaches for incorporating density functional theory (DFT)-based parameters of heme pairs into a quantum Liouville charge carrier model for these protein polymers, which includes transient quantum charge carrier features that may be crucial for predictive charge carrier modelling. The first, which we term spin-flip diabatization, relies on the properties of unrestricted DFT to extract site energies and inter-site couplings from canonical orbitals. This approach preserves the single site-orbital picture of each heme, but leaves out relaxation of the electron density. A second approach relies on linear-response equations from time-dependent DFT (TDDFT) to calculate adiabatic charge transfer states, including electronic relaxations by calculating energy differences and couplings via the excitation vector. We contrast the formalism of these two approaches, and discuss the behavior of the Liouville charge carrier model in the electron-hopping regime of weak coupling and large site energy differences.

Understanding the structure-property relationship of ACC-Dimers via high-throughput density functional theory and machine learning

Giacomo G. Nagaro,^a Luke Nambi Mohanam,^b Peter M. Mastracco,^c Sangram Prusty, ^a Younghoon Oh, ^a Qiang Cui, ^a Stacy Copp, ^{cde} Sahar Sharifzadeh^{bfa}

Department of Chemistry, Boston University^a Department of Electrical and Computer Engineering, Boston University^b Department of Materials Science and Engineering, University of California, Irvine^c Department of Chemical and Biomolecular Engineering, University of California, Irvine^d Department of Physics and Astronomy, University of California, Irvine^e Department of Physics, Boston University^f

We present an all-atom molecular dynamics (MD) and density functional theory (DFT) study of the explicitly solvated antiparallel coiled-coiled dimer (ACC), a self-assembled helical peptide bundle formed by two 29-residue α -helix peptide chains. ACC biofilms have been shown experimentally to efficiently conduct electricity and are therefore promising as components in synthetic bioelectronic materials. Classical MD under ambient conditions captures the thermal nuclear vibrations of this system. DFT calculations of 1000 MD snapshots of the ACC-Dimer with an explicit water solvation shell show near-degenerate frontier Kohn-Sham orbitals, which we expect to be the main driver of conductivity, that fluctuate with nuclear vibrations. Such a finding is consistent with a vibration-induced conductivity model. To understand this observation, we utilize feature analysis and machine learning algorithms to understand the relationship between nuclear geometry and the number of near-degenerate frontier orbitals. These results demonstrate the importance of a full atomistic picture for studying the electronic properties of supramolecular protein complexes.

Complete Computational Reaction Mechanism for Foldamer-Catalyzed Aldol Condensation

Reilly Osadchey Brown Boston University

Foldamers, small synthetic peptides made of alpha and beta-amino acids, have been found to be efficient catalysts for carbon-carbon bond-forming aldol reactions; of particular interest is their ability to catalyze macrocycle ring closure reactions. Kinetic measurements show that the rate of the reaction depends on the identity of the amine side chains present. However, such kinetic analyses and other characterization techniques (e.g mass spectrometry) can provide only limited and coarse-grained information regarding the overall mechanism and rate-determining step of foldamer catalysis. We use semiempirical density functional tight binding (DFTB) QM/MM metadynamics simulations to determine the free energy and transition state barrier for all elementary steps involved in the ring closure reactions. We have performed calculations for 44 elementary reaction steps, resulting in 2.7 microseconds of total simulation time to identify key trends regarding amine identity, and provide insight into the intermediates and rate-limiting step of the catalytic cycle.

Large-scale simulations of catalytic surface dynamics with first principles machine learning

Cameron J. Owen^{1, 2}

¹Department of Chemistry and Chemical Biology, Harvard University, Cambridge, Massachusetts 02138, United States ²John A. Paulson School of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts 02138, United States

Abstract

Understanding atomic-level processes in surface science and heterogeneous catalysis is complicated by the wide range of time scales and length scales needed for simulations. To accelerate molecular dynamics calculations, we rely on machine learning methods to capture interatomic interactions with quantum accuracy. We then implement and deploy these models on parallel GPUs to reach billions of atoms in size or microseconds in time, and demonstrate this scale for a Pt hydrogen exchange catalyst at the micron scale. One method is a family of equivariant interatomic potential models (NequIP [1] and Allegro [2]) based on symmetry-preserving layer architectures that we use to achieve state-of-the-art accuracy and training efficiency for simulating atomistic. Another method (FLARE [3, 4]) enables autonomous selection of training sets for reactive systems, based on adaptive closed-loop algorithm that constructs accurate and uncertainty-aware Bayesian force fields on-the-fly from a molecular dynamics simulation. We examine the current limitations of machine learning models across relevant metal systems [5] and highlight the usefulness of ML-accelerated MD simulations to study surface reconstruction [6], dislocation dynamics [7], direct heterogeneous reactions [4, 8], nanoparticle shape changes [9], and full-scale catalyst modeling. These results demonstrate the power of first-principles based machine-learned force fields for the dynamic study of a variety of material classes, yielding previously inaccessible mechanistic and kinetic insights at relevant scale for comparison to experimental characterization techniques.

References

- S. Batzner, A. Musaelian, L. Sun, M. Geiger, J. P. Mailoa, M. Kornbluth, N. Molinari, T. E. Smidt, and B. Kozinsky, Nature Communications 2022 13:1 13, 1 (2021).
- [2] A. Musaelian, S. Batzner, A. Johansson, L. Sun, C. J. Owen, M. Kornbluth, and B. Kozinsky, Nature Communications 14, 579 (2023).
- [3] J. Vandermause, S. B. Torrisi, S. Batzner, Y. Xie, L. Sun, A. M. Kolpak, and B. Kozinsky, npj Computational Materials 6, 20 (2020).
- [4] J. Vandermause, Y. Xie, J. S. Lim, C. J. Owen, and B. Kozinsky, Nature Communications 13, 5183 (2022).
- [5] C. J. Owen, S. B. Torrisi, Y. Xie, S. Batzner, K. Bystrom, J. Coulter, A. Musaelian, L. Sun, and B. Kozinsky, npj Computational Materials 10, 92 (2024).
- [6] C. J. Owen, Y. Xie, A. Johansson, L. Sun, and B. Kozinsky, Nature Communications 15, 3790 (2024).
- [7] C. J. Owen, A. D. Naghdi, A. Johansson, D. Massa, S. Papanikolaou, and B. Kozinsky, arXiv preprint arXiv:2401.04359 (2024).
- [8] A. Johansson, Y. Xie, C. J. Owen, J. S. Lim, L. Sun, J. Vandermause, and B. Kozinsky, arXiv preprint arXiv:2204.12573 (2022), 10.48550/arxiv.2204.12573.
- [9] C. J. Owen, N. Marcella, Y. Xie, J. Vandermause, A. I. Frenkel, R. G. Nuzzo, and B. Kozinsky, arXiv:2306.00901 (2023), 2306.00901 [cond-mat.mtrl-sci].

Real-time dynamics of spin, orbit, charge via time-dependent density functional theory: Ab initio access to geometric or topological natures of solid states

Noejung Park, Ulsan National Institute of Science and Technology (UNIST), Department of Physics, UNIST-gil 50, Ulsan, 44919 Korea

We have performed the real-time time-dependent density-functional theory calculations, mostly within the adiabatic local density approximation(ALDA), to access to various Berry-curvature characteristics of solid states. We demonstrate that the quantum anomalous Hall conductivity and the quantum spin Hall conductivity of real-material bulk topological insulators can be directly obtained through the real-time profile of the electrons velocity. We extend our methods to nonlinear optical responses associated with spin-orbit dynamics, particularly focusing on the situation when a built-in geometrical chirality is linked to an electric field and/or magnetic field with even a non-zero topological term $\mathbf{E} \cdot \mathbf{B}$. We show that the spin structure emerging over the charge-orbit dynamical state has a quite different characters from the models commonly cited in the interpretations of experimental results. The analogy of these real-time dynamics with the Thouless pump model in the extreme adiabatic limit and the possible realization of axial anomaly as a lattice gauge theory are also discussed. This talk also includes the limitation and utility of ALDA of the exchange-correlation magnetic field in for the aforementioned spin-orbit dynamics.

<u>Title</u>: Pseudo-atomic orbital based tight-binding model investigation of Fermi Arcs in Na₃Bi.

<u>Name</u>: Vasilios Passias and Lucas Wagner <u>Affiliation</u>: University of Illinois at Urbana-Champaign

Na₃Bi is a topological Dirac semimetal [1] whose double surface Fermi arcs were initially thought to be topologically protected [1-3]. Angle resolved photoemission spectroscopy (ARPES) measurements on Na₃Bi's (100) facet [4] are consistent with double surface Fermi arcs [1,2]. However, it was shown that bulk symmetry preserving terms that leave the Dirac points unchanged could deform the double surface Fermi arcs into a closed Fermi contour that does not connect to the Dirac points [5] and could be still consistent with the ARPES data.

We investigate how robust the double surface Fermi arcs are to Na_3Bi (100) slabs with different terminations. We construct tight binding models of two Na_3Bi (100) slabs using pseudo-atomic orbitals [6]. Away from the projected Dirac points we find slab termination localized states. Near the projected Dirac points there is a hybridization of surface and bulk states. Both findings are consistent with the predicted behavior of Fermi arcs in Na_3Bi . We find that while the arcs are not strictly topologically protected, they are quite robust for realistic surfaces.

<u>Funding</u>: We thank the Illinois Physics department for funding. <u>Computational Resources</u>: We thank the Illinois Campus Cluster for computational resources.

1. Z. Wang, et al, Phys. Rev. B 85, 195320 (2012).

- 2. A. C. Potter, I. Kimchi, and A. Vishwanath, Nature Communications 5, 5161 (2014).
- 3. E. V. Gorbar, V. A. Miransky, I. A. Shovkovy, and P. O. Sukhachov, Phys. Rev. B 91, 121101 (2015).
- 4. S.-Y. Xu, et al, Science 347 (2015).
- 5. M. Kargarian, M. Randeria, and Y.-M. Lu, Proceedings of the National Academy of Sciences 113 (2016).
- 6. M. Buongiorno Nardelli, et al, Computational Materials Science 143 (2018).

Application of first-principle electronic free energy calculations to bond breaking in the nitrogen dimer

William Z. Van Benschoten¹, Hayley R. Petras², and James J. Shepherd¹ ¹Department of Chemistry, Michigan State University, East Lansing, Michigan 48824, USA ²Department of Chemisty, University of Iowa, Iowa City, Iowa 52242, USA

Using the free-energy Born—Oppenheimer (FEBO) approximation we calculate the free energy (F) surface for the nitrogen dimer, a benchmark system. We use exact finite temperature full configuration interaction (ft-FCI) method in a minimal basis, and density matrix quantum Monte Carlo calculations for larger basis sets. Considering only the internal energy (U) surface one finds a counterintuitive bond strengthening at temperatures T>0. However, when considering the free-energy surface, we see only a gradual bond weakening with increasing T. This gradual bond weakening is caused by the thermally scaled entropic (-TS) component for F which counteracts the behavior in U. Using the free-energy surface, we can calculate a dissociation temperature, and find this temperature is below the experimentally measured dissociation energy. We explore the impact that the determinant space has on our calculated dissociation temperature and determine that including more symmetries for the determinant space lowers the calculated dissociation temperature. We also investigate the basis set dependence for the dissociation temperature and find that using a larger basis set increases the dissociation temperature.

We explore the origins for the free-energy surface behaviors using histograms for the density matrix and find that the longer bond length density matrix is more sensitive to changes in temperature.

Research was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences Early Career Research Program (ECRP) under Award Number DESC0021317. Computer resources for this project were also provided from the University of Iowa and the National Energy Research Scientific Computing Center, a DOE Office of Science User Facility supported by the Office of Science of the U.S. Department of Energy under Contract No. DE-AC02- 05CH11231 using NERSC award BES-ERCAP0019952.

Half-semimetallicity in graphene nanoribbon/hexagonal boron nitride heterojunctions

Michele Pizzochero,¹ Nikita V. Tepliakov,² Ruize Ma,³ Johannes Lischner,² Arash A. Mostofi,² E. Kaxiras¹

¹Harvard University, ² Imperial College London, ³ University of Oxford

Half-metals have been envisioned as active components in spintronic devices by virtue of their completely spin-polarized electrical currents. Actual materials hosting half-metallic phases, however, remain scarce. Using first-principles calculations, we predict that recently fabricated heterojunctions of zigzag nanoribbons embedded in two-dimensional hexagonal boron nitride are half-semimetallic, featuring fully spin-polarized Dirac points at the Fermi level. The half-semimetallicity originates from the transfer of charges from hexagonal boron nitride to the embedded graphene nanoribbon. These charges give rise to opposite energy shifts of the states residing at the two edges, while preserving their intrinsic antiferromagnetic exchange coupling. We further propose a simple mean-field Hubbard model Hamiltonian to capture the essential physics. Our findings demonstrate that these heterojunctions realize tunable one-dimensional conducting channels of spin-polarized Dirac fermions seamlessly integrated into a two-dimensional insulator, thus holding promise for the development of carbon-based spintronics.

N. V. Tepliakov, R. Ma, J. Lischner, E. Kaxiras, A. Mostofi, M. Pizzochero, Nano Lett. 23, 6698 (2023)

This work is supported by the STC Center for Integrated Quantum Materials, National Science Foundation Grant No. DMR-1231319 and the National Science Foundation under Award No. DMR-1922172.

Probing non-equilibrium dynamics in correlated materials with first-principles-based timedependent microscopic models

Sangeeta Rajpurohit Lawrence Berkeley National Laboratory

The interaction between charge, spin, and lattice degrees of freedom in strongly correlated systems under external stimuli leads to several intriguing phenomena. High-resolution ultrafast pump-probe spectroscopy experiments in these materials have uncovered fascinating physical effects, such as photoinduced phase transitions, photovoltaic effects, and transient "hidden" phases. However, the fundamental mechanisms behind these photoinduced processes, which are vital for practical applications, remain largely unknown. A detailed microscopic understanding of the energy conversion processes is crucial. Theoretical investigation of these processes is complex and requires methods capable of addressing the large spatiotemporal scales of various active degrees of freedom. I will discuss the first-principles-based microscopic modeling of relaxation dynamics in materials and present simulation results for correlated oxides, emphasizing the role of spin and phonons in photo-induced dynamics. In the charge-ordered stripe phase, photoinduced phase transitions can be highly selective based on the light pulse's intensity and polarization. I will present simulation results on the generation and evolution of photocurrent, along with strategies to enhance the photovoltaic response in strongly interacting ferroelectric systems. I will also briefly highlight possible spin- and lattice-assisted relaxation mechanisms.

References:

1) S. Rajpurohit, C.D. Pemmaraju, T. Ogitsu, L.Z. Tan. PRB, 105, 094307 (2022)

2) S. Rajpurohit, L.Z. Tan, C. Jooss, P.E. Blöchl. PRB 102 (17), 174430 (2020)

3) M. Sotoudeh, S. Rajpurohit, P.E. Blöchl et al. PRB 95 (23), 235150 (2017)

Exploring phonon-magnon band structures for CrI₃: Fundamental calculations, topological properties, and thermal Hall effect implications

Shang Ren,¹ Miquel Royo,² Massimiliano Stengel,^{2,3} and David Vanderbilt¹ ¹ Department of Physics and Astronomy, Rutgers University, Piscataway, New Jersey 08854, USA ² Institut de Ciència de Materials de Barcelona (ICMAB-CSIC), Campus UAB, 08193 Bellaterra, Spain ³ ICREA-Institució Catalana de Recerca i Estudis Avançats, 08010 Barcelona, Spain

While phonon and magnon bands can traditionally be calculated by diagonalizing the dynamical matrix and solving the Landau-Lifshitz equation, respectively, the study of band structures that incorporate phonon-magnon interactions is still in its infancy. In our recent work [1,2], we have developed a method that treats phonons and magnons on an equal footing, focusing on zone-center modes. We are currently extending this approach to finite momenta, utilizing both the finite-difference method and a recently developed density-functional perturbation theory approach [3].

In this presentation, we will showcase the phonon-magnon band structures for both bulk and monolayer CrI_3 , highlighting numerous anti-crossing points. We will demonstrate the calculation of the Chern number and confirm the existence of non-trivial topology in the magnon bands. Additionally, we will address the puzzle of the magnon Dirac gap observed in inelastic neutron scattering experiments and provide our insights into this phenomenon. Finally, we will discuss the implications of our method for understanding the thermal Hall effect.

Reference:

Shang Ren, John Bonini, Massimiliano Stengel, Cyrus E. Dreyer, and David Vanderbilt, Adiabatic Dynamics of Coupled Spins and Phonons in Magnetic Insulators, Phys. Rev. X 14,011041 (2024)
 John Bonini, Shang Ren, David Vanderbilt, Massimiliano Stengel, Cyrus E Dreyer, Sinisa Coh, Frequency Splitting of Chiral Phonons from Broken Time-Reversal Symmetry in CrI₃, Phys. Rev. Lett. 130, 086701 (2023)

[3] Miquel Royo and Massimiliano Stengel, unpublished

The Real-time Dyson Expansion: Efficient Inclusion of Dynamical Correlations in Non-equilibrium Spectral Properties

Presenter: Cian Charles Reeves PI: Vojtech Vlceck University of California Santa Barbara

A key experimental technique for probing real-time non-equilibrium dynamics of electronic states is timeresolved photoemission spectroscopy. Predicting this time-resolved spectra theoretically represents a challenge, in particular in realistic systems. The Kadanoff-Baym equations provide one route to computing the two-time Green's function and thus the time-resolved spectrum,, however the resulting computation scales cubically in the number of time steps, thus quickly becoming prohibitively expensive. Using a meanfield approach fixes the problem of scalability with only a linear cost in the number of time steps. The cost of this reduced scaling is that mean-field methods neglect dynamical correlation effects and miss key spectral properties such as emergent spectral features. We present a new technique we have developed that allows for the inclusion of dynamical correlation effects while maintaining the same numerical scaling in the number of time steps as a mean-field approach. Further, the scheme generalizes a commonly applied equilibrium method that has had great success in practical ab-initio many-body perturbation theory. The method shows excellent agreement with exact results in test systems. Additionally we exemplify the scalability of the method on a periodic system and demonstrate clear evidence that our proposed scheme produces complex spectral features including excitonic band replicas, features that are not observed using static mean field approaches.

Unveiling the evolution of charge density wave order in twisted bilayers of NbSe₂: A Machine-Learning approach

Norma Rivano¹, Zachary Goodwin¹, Francesco Libbi¹, Chuin Wei Tan¹, and Boris Kozinsky¹

¹Jhon A. Paulson School of Engineering and Applied Sciences, Harvard University, Cambridge, MA 02138, USA

Niobium diselenide has garnered significant interest over the past decade due to the coexistence of superconductivity and a charge density wave (CDW), which have been experimentally observed down to the monolayer limit. Their coexistence, and evolution with varying numbers of layers and different twisting angles are central topics in twistronics and would benefit from accurate atomistic simulations. However, traditional first-principles methods fall short due to the large number of atoms needed to accommodate the long-wavelength moiré pattern. This study adopts a practical approach by leveraging ab initio data to develop accurate machine learning interatomic potentials thanks to the ALLEGRO architecture, an open-source code for building highly scalable and accurate equivariant deep learning interatomic potentials. We explore the formation and evolution of CDW order in monolayers and twisted bilayers. Our results are validated against density functional theory calculations, encompassing structural relaxation and phonon dispersions, with minimal errors observed in energy and forces.

Molecules as Neural Networks

Sol Samuels^{1,2} and Susan R. Atlas^{1,3,4} Departments of Physics & Astronomy, Mathematics & Statistics, Chemistry & Chemical Biology, and Center for Quantum Information and Control University of New Mexico, Albuquerque, NM 87131

Given a quantum mechanical electron density for a molecule, an atom-in-molecule (AIM) decomposition partitions the molecular system into constituent atomic-like entities. This decomposition is not unique, and various theoretical methods have been proposed for defining chemically-reasonable AIMs. We describe the use of machine learning techniques, specifically radial basis function neural networks (RBF-NNs), to analyze molecular electron density distributions as AIM DFT ensemble decompositions [1]. The RBF-NN is designed to directly represent the AIM ensemble framework in terms of weighted superpositions of electron densities for individual ground, excited and charge states of the constituent atoms [2]. The neural network optimizes the electron density weights, while enforcing physical constraints, to define the contributions of individual atomic states to the overall molecular density. Our approach relies on universal function approximation theorems for neural networks [3].

We present results for LiF as an exemplar of ionic bonding and discuss insights into different bonding regimes derived from the neural network representation. Remarkably, we find that the RBF-NN can detect the transition from the ionically-bound molecule to isolated neutral atoms as a function of internuclear separation, *R*, independent of the level of theory. This is despite the fact that the levels of theory used to train the neural network fail to detect the transition via the computed dipole moment. The location of the transition is shown to depend on the level of theory. DFT models more equipped to represent charge transfer, such as wB97XD [4], locate the transition closer to the highly accurate quantum chemical results of Varandas [5]. This suggests that the quantum mechanical bonding information is intrinsic to the molecular electron density and transcends the exchange-correlation energy model used to compute it.

The RBF-NN framework provides a deeper understanding of contributions of individual atoms and atomic states to molecular properties and interactions, as a function of molecular structure. This includes bond formation and breaking – transitioning from isolated neutral atoms to chemical bonds – and the development of reactive charge transfer potentials for dynamical simulations [6].

Support from the NSF and from NSF REU grant #PHY-1659618 is gratefully acknowledged. We thank the UNM Center for Advanced Research Computing (CARC) for computational support.

References

- [1] S.R. Atlas. "Embedding quantum statistical excitations in a classical force field," J. Phys. Chem. A,
 - **125**, 3760 (2021); K. Muralidharan, S.M. Valone, and S. R. Atlas. "Environment dependent charge potential for water," arXiv:0705.0857 [cond-mat.mtrl-sci] (2007).
- [2] G. Amo-Kwao and S. R. Atlas, "Radial basis function electron densities with asymptotic constraints," ms., University of New Mexico (2024).
- [3] K. Hornik, "Multilayer feedforward networks are universal approximators," Neural Networks 2, 359 (1989).
- [4] J.-D. Chai and M. Head-Gordon, "Systematic optimization of long-range corrected hybrid density functionals," J. Chem. Phys. 127, 084106 (2008); J.-D. Chai and M. Head-Gordon, "Long-range corrected hybrid density functionals with damped atom-atom dispersion corrections," Phys. Chem. Chem. Phys. 10 (2008) 6615-20 (2008).
- [5] AJC Varandas, J. Chem. Phys. 131, 124128 (2009).
- [6] C.M. Baxter, S.M. Valone, and S.R. Atlas. "Ensemble embedding functions for atomistic dynamics," ms. (2024).

Towards more complete *ab initio* calculations of the bulk photovoltaic effect

Aaron M. Schankler University of Pennsylvania

The bulk photovoltaic effect (BPVE) is a process through which a homogeneous but noncentrosymmetric material can generate a photocurrent in the bulk. This response can facilitate sensitive, self-powered detectors, and can also generate above-bandgap photovoltages, which can increase the power conversion efficiency of photovoltaic devices. The effect is usually described in terms of two mechanisms: the ballistic current, where asymmetric scattering leads to unequal carrier generation rates at opposite momenta, and the shift current, where carrier excitation is accompanied by a net displacement in real space. The shift current is well described theoretically, and its deep connection to electronic band geometry provides important insight into quantum materials. However, the shift current alone does not fully explain experimental observations of the BPVE. Accordingly, we discuss first-principles methods for calculating ballistic current arising from electron-phonon scattering that, together with the shift current, provides a better description of experiment.

However, the story does not stop at excitation: photoexcited carriers relax and recombine, forming a kinetic cycle at steady state. The relaxation and recombination processes are also predicted to produce photocurrent through a shift current mechanism, but so far, they have only been calculated in model systems. Thus, it is difficult to know the relative magnitude of the relaxation currents in comparison to the more commonly calculated excitation currents. To address this gap, we model photocurrents arising from carrier recombination from first principles. We find that even in a simple material, quantitative calculations are required to account for the sometimes-competing contributions from different bands, which can lead to very different responses under different experimental conditions. This capability will be even more important when studying materials with more complex electronic structure, nonzero magnetism, or nontrivial topology.

Inducing topological flat bands in bilayer graphene with electric and magnetic superlattices

Daniel Seleznev¹, Jennifer Cano², and David Vanderbilt¹

¹Department of Physics and Astronomy, Center for Materials Theory, Rutgers University, Piscataway,

New Jersey 08854, USA

²Department of Physics and Astronomy, Stony Brook University, Stony Brook, New York 11794, USA

It was recently argued that Bernal stacked bilayer graphene (BLG) exposed to a 2D superlattice (SL) potential exhibits a variety of intriguing behaviors [1]. Chief among them is the appearance of flat Chern bands – with the possibility of Chern numbers C such that |C| > 1 – that are favorable to the appearance of fractional Chern insulator states. Here, we explore extensions of the model of Ghorashi et al. [1] to find additional means of inducing flat Chern bands. We focus on the effects of out-of-plane orbital magnetic fields due to their tendency to flatten bands and induce band topology. In particular, we study fields that vary on length scales much larger than the atomic spacing in BLG, generating what we refer to as magnetic SLs. The magnetic SLs we investigate either introduce no net magnetic flux to the SL unit cell, or a single quantum of flux; in the latter case we employ a recently developed gauge-independent formalism to diagonalize the resulting magnetic continuum Hamiltonian [2]. We find that magnetic SLs on their own can induce flat bands with |C|>1, but richer behavior featuring multiple topological flat bands with |C| > 1 can be observed when the magnetic SLs act in conjunction with commensurate electric SLs. Finally, we propose a method of generating flux quantum magnetic SLs along with concomitant electric SLs. The magnetic SL is generated by periodic arrays of flux vortices originating from type II superconductors, while the electric SL arises due to a magnetic SL-induced charge density on the surface of a magnetoelectric material. Tuning the vortex lattice and the magnetoelectric coupling permits control of both SLs, and we study their effects on the band structure of BLG.

S. A. A. Ghorashi et al., Phys. Rev. Lett. **130**, 196201 (2023).
 J. Herzog-Arbeitman et al., Phys. Rev. B **106**, 085140 (2022).

Altermagnetism from first principles

Yujia Teng Department of Physics and Astronomy, Rutgers University, New Brunswick, New Jersey 08901, USA

Antiferromagnetism (AFM) is one of the most common types of magnetic ordering. AFM states have zero macroscopic magnetization due to cancellation of individual moments in the unit cell. The electronic bands of many antiferromagnets are doubly degenerate if spin-orbit coupling is neglected. However, this requires the presence of a particular symmetry operation. Recently, it has been recognized that there is a type of antiferromagnetism, called altermagnetism, in which the bands at a general k point are spin split even when spin-orbit coupling is neglected. In this poster, I will explain what altermagnetism is, and the symmetry criterion for a particular system to be altermagnetic. I will present representative examples including results from my current work on altermagnetism.

Spatial-dispersive optical phenomena in crystalline solids: an *ab initio* approach based on Wannier interpolation

Andrea Urru¹, Oscar Pozo Ocaña^{2,3}, Stepan S. Tsirkin^{2,3}, Ivo Souza^{2,3}, and David Vanderbilt¹

¹Department of Physics and Astronomy, Center for Materials Theory, Rutgers University, Piscataway, New Jersey 08854, USA

² Centro de Física de Materiales, Universidad del País Vasco, 20018 San Sebastián, Spain.
³ Ikerbasque Foundation, 48013 Bilbao, Spain.

When electromagnetic waves interact with a periodic solid, a number of interesting phenomena can take place, according to the symmetry properties of the crystalline solid. Among them we mention, e.g., linear birefringence and dichroism, the Faraday effect, natural optical activity (rotatory power and circular dichroism), gyrotropic birefringence, and non-reciprocal dichroism. Such phenomena are encoded in the frequency- and momentum-dependent optical conductivity linear response $\sigma_{\alpha\beta}(\omega, \mathbf{q})$. Upon expansion in powers of the wave vector \mathbf{q} of the incident light, $\sigma_{\alpha\beta}(\omega, \mathbf{q})$ reads

$$\sigma_{\alpha\beta}(\omega, \mathbf{q}) = \sigma_{\alpha\beta}^{(0)}(\omega) + \sigma_{\alpha\beta,\gamma}(\omega)q_{\gamma} + \mathcal{O}(q^2),$$

with a sum over γ implied. The zeroth-order term $\sigma_{\alpha\beta}^{(0)}(\omega)$ describes linear birefringence and dichroism, as well as the Faraday effect, which are present even in centrosymmetric periodic solids. On the other hand, the first-order term $\sigma_{\alpha\beta,\gamma}(\omega)$ captures spatial-dispersive phenomena, such as natural optical activity in acentric non-magnetic materials, as well as gyrotropic birefringence and non-reciprocal dichroism in acentric antiferromagnets.

Recently, an approach for the calculation of the aforementioned spatial-dispersive optical conductivity, based on a Kubo formulation, has been proposed [1]. In this work, we present an implementation of this theoretical framework using Wannier interpolation. This technique is particularly well-suited for treating interband optical transitions because these require a fine sampling in reciprocal space to obtain a well-resolved spectrum, a requirement that is hard to meet with direct *ab initio* calculations. Furthermore, we test our implementation with some benchmark calculations. In particular, we compute the circular dichroism of GaN and the rotatory power of trigonal Te and compare our results to those obtained in Ref. [2] at a similar level of theory as ours, as well as previous experimental measurements [3,4]. We also compute the rotatory power of trigonal Se and discuss our results in light of the substantial effect of local fields recently addressed in Ref. [5] from a density functional perturbation theory standpoint.

- [1] O. Pozo Ocaña and I. Souza, SciPost Phys. 14, 118 (2023)
- [2] X. Wang and Y. Yan, Phys. Rev. B 107, 045201 (2023).
- [3] S. Ades and C. H. Champness, J. Opt. Soc. Am. 65, 217 (1975).
- [4] S. Fukuda, T. Shiosaki, and A. Kawabata, Phys. Status Solidi B 68, K107 (1975).
- [5] A. Zabalo and M. Stengel, Phys. Rev. Lett. 131, 086902 (2023).

Basis set convergence for first-principle electronic free energy calculations

William Z. Van Benschoten and James J. Shepherd Department of Chemistry, Michigan State University, East Lansing, Michigan 48824, USA

We investigated the basis set size (M) dependence for finite temperature quantities in the canonical ensemble using the exact ft-FCI method. Studies are conducted for the uniform electron gas (UEG) and helium using a plane-wave basis, and this is contrasted with an isolated hydrogen atom. Several of the convergence behaviors are related to the momentum distribution (n(q)) and static structure factor (S(q)). In the canonical ensemble for T>0, the free energy can be a variational quantity with M, rather than U. We find that the free-energy convergence for warm to low T matches the known U(T=0) convergence rates of $M^{(-1)}$ for unpolarized and $M^{(-5/3)}$ for fully polarized systems.

Research was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences Early Career Research Program (ECRP) under Award Number DESC0021317. Computer resources for this project were also provided from the University of Iowa.

Quantum Dynamics of Coupled Electron-Proton Systems in Heterogeneous Environments Using the Nuclear-Electronic Orbital Method

Jianhang Xu¹, Ruiyi Zhou¹, Zhen Tao³, Tao E. Li³, Volker Blum^{5,6}, Sharon Hammes-Schiffer^{3,4}, and Yosuke Kanai^{1,2}

 ¹Department of Chemistry, the University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27599, USA
 ²Department of Physics and Astronomy, the University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27599, USA
 ³Department of Chemistry, Yale University, New Haven, Connecticut 06520, USA
 ⁴Department of Chemistry, Princeton University, Princeton, New Jersey 08544, USA
 ⁵Thomas Lord Department of Mechanical Engineering and Material Science, Duke University, Durham, North Carolina 27708, USA
 ⁶Department of Chemistry, Duke University, Durham, North Carolina 27708, USA

Accurate modeling of catalytic processes in complex heterogeneous environments often requires the quantization of protons in electronic structure calculations. The nuclear-electronic orbital (NEO) method treats nuclei quantum mechanically beyond the Born-Oppenheimer approximation. We developed and implemented the NEO method for periodic electronic structure calculations using multicomponent density functional theory (DFT) in the all-electron code FHI-aims. This method, validated through applications to systems like trans-polyacetylene chains and titanium oxide-water interfaces, demonstrates that quantized protons impact the density of states and band structures of these materials.

We also present a new periodic real-time nuclear-electronic orbital time-dependent density functional theory (RT-NEO-TDDFT) method for treating electron and proton dynamics quantum mechanically. This implementation in FHI-aims utilizes analytical and numerical integration techniques to enhance computational efficiency. RT-NEO-TDDFT was applied to investigate how heterogeneous environments, such as solvating waters and material surfaces, impact electronically excited-state processes. Using o-hydroxybenzaldehyde as a case study, we illustrate how these environments influence the balance between quantum-mechanical proton transfer and electronic excitation dynamics.

Additionally, RT-NEO-TDDFT with Ehrenfest dynamics was developed to study coupled electronproton dynamics in more complex environments with significant nuclear movement. This method provides a robust framework for studying quantum dynamic processes, such as proton-coupled electron transfer in heterogeneous systems, offering insights into key reaction steps in the catalytic cycle for solar-to-fuel energy conversion.

Multipole Representations of Spin-Splitting Hamiltonians in Non-Magnetic Crystals

Fan Yang¹ (presenter), Rafael M. Fernandes², Turan Birol¹ ¹Department of Chemical Engineering and Materials Science, University of Minnesota ²School of Physics and Astronomy, University of Minnesota

Understanding the details of the spin-polarization in materials is necessary for technological applications that require exploiting the electronic spin degree of freedom. In non-magnetic systems that preserve time-reversal symmetry (T), when spatial inversion (I) is absent, the spin degeneracy of the crystal's electronic band spectrum can be lifted in the reciprocal space due to spin-orbit coupling (SOC), with each spin-free electronic band split into two spin-polarized subbands with opposite spin states. Such T-even spin-polarized pattern in the k-space is governed by crystallographic symmetries, just like many other physical properties of materials. However, there are totally 21 non-centrosymmetric (NCS) crystallographic point groups that lack I, each holding a distinct spin pattern in reciprocal space [1]. This leads to the questions: How can we understand the differences of T-even spin patterns in different NCS point groups? Is it possible for us to sort them into a complete basis and represent their symmetry properties in an intuitive way?

Our solution is to describe the SOC-induced spin-splitting effects in the framework of electric (E) and electric toroidal (ET) multipoles, which together form a complete and infinite basis for any *T*-even properties from the symmetry aspect [2]. Starting from the non-magnetic centrosymmetric parent point group $m\overline{3}m(O_h)$, we apply group theoretical analysis on all possible, lowest-order *T*-even SOC Hamiltonians. We classify them into six classes according to how they transform under symmetries and construct isomorphic E/ET-multipole representation in the parent point group for each class. We justify our theory by building up real-space tight-binding (TB) models with different local charge multipoles in presence and fit the resultant spin-polarized pattern to corresponding *k*-space SOC Hamiltonian, finding excellent agreement between them. For interesting and less-discussed cases, we also provide real-materials example of band spectrum using density functional theory (DFT). For completeness, we also carry out analysis within hexagonal setting for subgroups of 6/mmm (D_{6h}) using the same workflow. Our work provides a systematic classification of *T*-even spin-splitting Hamiltonians. Instead of directly working with the 21 NCS crystallographic point groups, we project any possible SOC Hamiltonian onto a full basis of E/ET-multipoles, such that the SOC Hamiltonian is a linear combination of basis terms allowed in the given point group, with the contribution strength indicated by associated coefficients.

References:

[1] Samokhin, K. V. (2009). Annals of Physics, 324(11), 2385–2407.

[2] Hayami, S., Yatsushiro, M., Yanagi, Y., & Kusunose, H. (2018). *Physical Review B*, 98(16), 165110.

Low-scaling algorithms for many-body electronic structure and downfolding for quantum embedding

Chia-Nan Yeh, Miguel Morales Center for Computational Quantum Physics, Flatiron Institute

Quantum embedding has become one of the most successful techniques for materials simulations due to its multilayer treatments for different physical scales. Aside from the need of efficient solvers for the strongly correlated subspace, constructing a material-specific low-energy Hamiltonian beyond density functional theory (DFT) requires an efficient many-body method for the weakly correlated environment. In this talk, I will report our recent efforts on the low-scaling algorithms for many-body electronic structure and downfolding based on tensor hypercontraction (THC). THC is a systematically controlled compression technique for generic many-body Hamiltonians in any canonical basis. The resulting representation of the many-body Hamiltonians exhibits desired separability in the orbital and k-points indices which leads to the constructions of low-scaling algorithms for the following many-body calculations. We demonstrate the applicability and efficiency of THC in the context of downfolding procedures, including GW electronic structure and constructing low-energy Hamiltonian beyond DFT for large-scale systems.

All-electron BSE@GW method for Extended Systems with Numeric Atom-Centered Orbitals

Ruiyi Zhou¹, Yi Yao², Xinguo Ren³, Volker Blum^{4,5}, and Yosuke Kanai^{1,6}
1. Department of Chemistry, University of North Carolina at Chapel Hill
2. The NOMAD Laboratory at the FHI-MPG and IRIS-Adlershof of HU,Berlin
3. Institute of Physics, Chinese Academy of Sciences
4. Department of Chemistry, Duke University
5. Thomas Lord Department of Mechanical Engineering and Materials Science, Duke University
6. Department of Physics and Astronomy, University of North Carolina at Chapel Hill

Abstract

Green's function theory has emerged as a powerful many-body approach not only in condensed matter physics but also in quantum chemistry in recent years [1,2]. We have developed a new all-electron implementation of the BSE@GW formalism using numeric atom-centered orbital basis sets. We present our recent developments in implementing this formalism for extended systems with the periodic boundary conditions [3]. We will discuss its implementation and numerical challenges. We will present various convergence tests pertaining to numerical atomic orbitals, auxiliary basis set for the resolution-of-identity formalism, and Brillouin zone sampling, etc. Several proof-of-principle examples will be presented to compare with other formalisms, illustrating the new all-electron BSE@GW method for extended systems.

Reference:

- 1. Ren, Xinguo, et al. "All-electron periodic G0W0 implementation with numerical atomic orbital basis functions: Algorithm and benchmarks." *Physical Review Materials* 5.1 (2021): 013807.
- 2. Yao, Yi, et al. "All-electron BSE@ GW method for K-edge core electron excitation energies." *Journal of Chemical Theory and Computation* 18.3 (2022): 1569-1583.
- 3. Zhou, Ruiyi, et al. "All-electron BSE@GW method with Numeric Atom-Centered Orbitals for Extended Systems." In preparation.

Higher-dimensional spin selectivity in chiral crystals

Yinong Zhou University of California, Irvine

The chiral-induced spin selectivity effect has attracted significant attention in interdisciplinary research fields due to its potential to offer pure spin currents without requiring magnetic fields or materials. Previous studies have neglected the spin selectivity in the normal plane of chiral molecules and crystals because the chiral-induced spin-orbit coupling (CISOC) strength is assumed to be substantially stronger than the antisymmetric SOC (ASOC) terms. This poses a challenge in chiral van der Waals crystals like indium selenoiodide (InSeI) that consists of heavy elements in a bundle of atomically precise 1D helical chains. This study aims to investigate the interplay between CISOC along the screw axis and ASOC in the normal plane within a chiral crystal, using both general model analysis and first-principles simulations. Using InSeI as a showcase, we reveal a three-dimensional (3D) spin selectivity in chiral crystals. The resulting phase diagram of spin accumulation shows the potential for controlling phase transition and flipping spin by reducing symmetry through surface cleavage, thickness reduction, or strain. We also experimentally synthesized high-quality InSeI crystals of the thermodynamically stable achiral analogue, which showed exposed (110) facets corresponding to single-handed helices to demonstrate the potential of material realization for higher-dimensional spin selectivity in the development of spintronic devices.

Simulation of energy flow in femtosecond-laser excited h-BN/graphene heterostructures

<u>Tobias Zier</u>¹, Arne Ungeheuer², Ahmed Hassanien², Thomas Baumert²,

Arne Senftleben², David A. Strubbe¹

¹ Department University of Physics, University of California Merced, Merced, CA 95343, USA

² University of Kassel, Institute of Physics and CINSaT, 34132 Kassel, Germany

tzier2@ucmerced.edu

Recent years show increasing interest in 2D vdW materials after unique properties as well as new effects in those materials were observed. Phenomena linked to heterostructures are, but not limited to, interlayer excitons, new phonon modes, band structure hybridization or Moiré superlattice effects such as unconventional superconductivity. A promising way to induce but also investigate new processes in 2D vdW heterostructures is femtosecond-laser pulses because of their pulse duration comparable to typical time scales of atomic motions in molecules and solids. Additionally, the ability to shape amplitude, phase, and polarization within one pulse provides a variety of excitation channels. More general, the excitation of a crystalline material by an intense ultrashort-laser pulse creates extreme nonequilibrium conditions within the solid. The optical energy of such an excitation is, due to the high difference in mass of electrons and atoms, mainly deposited in the electronic system. Therefore one can induce electronic temperatures in materials of several 10000's of K, whereas the atomic system remains almost unaffected near room temperature. Such an immense change in the electronic system has a direct influence on the bonding properties of the material and is the origin of several ultrafast phenomena. But how is the deposited energy distributed after the excitation within the material and on which timescale? The answer to this question becomes even harder in the case of 2D vdW heterostructures. Why? Compared to, e.g., silicon inter-material correlations of electrons and phonons in vdW heterostructures, like h-BN/graphene, open interaction and energy diffusion channels that might not be present in either of the single materials. Recent research showed, e.g., out-of-plane heat transfer by electron-hyperbolic phonon coupling or ultrafast relaxation of hot phonons. In order to investigate the strength and direction of energy flow within and between heterostucture layers after a femtosecond-laser excitation we performed ab initio calculations of mono-layer hBN-graphene using the real-space and real-time density-functional-theory (DFT) code Octopus. The laserpulse excitation is simulated by an time-dependent vector potential with a Gaussian shaped envelope. The now time-dependent response of the electron density is computed with time-dependent DFT (TDDFT). The characterizing parameters of the corresponding electrical field are the amplitude A = 0.072836 eV/Å that corresponds to a peak intensity of 7.04×10^{10} W/cm², the wavelength 800 nm corresponds to $\hbar\omega = 1.549$ eV, and the pulse duration t = 25 fs. The timestep for the electronic evolution is t = 0.33 as. The induced ionic motion by the changing electronic system is computed in accordance to Ehrenfest dynamics. Note that hBN is transparent for the used wavelength of 800 nm: it does not absorb laser-pulse energy, whereas graphene/graphite does. In this setup we assure that only the electronic system of carbon-based subsystem is excited so that the ensuing energy flow into different channels can be identified and quantified. Our findings allow us to give a theoretical picture on the thermalization process within both materials but also between them. Moreover, by comparing our simulation results to experimentally obtained time-resolved ultrafast-electron-diffraction data we are enabled to verify our theoretical predictions but also improve our theoretical approach to a point where reliable prediction to thermal and non-thermal contributions and their corresponding timescales can be obtained. Those results are an important step towards understanding of inter-material correlations which can be used to control the ensuing structural response.